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Melt processable copolyimides based on 4,4′-bis(3-aminophenoxy)biphenyl

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Copolyimides based on 4,4′-bis(3-aminophenoxy)biphenyl (abbreviated to BAB) and pyromellitic dianhydride (PMDA) were synthesised with 4,4′-oxydianiline (4,4′-ODA) and/or 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA). Basic property and melt processability of synthesised copolyimides were investigated. Crystallisation property of these copolyimides were dependent on contents of 4,4′-ODA and/or BPDA. Melt processability of copolyimides obtained from BAB, 4,4′-ODA and PMDA were dependent on contents of 4,4′-ODA. Melt viscosities and *Tg*'s of copolyimides obtained from BAB, PMDA and BPDA were decreased according to increase of BPDA contents. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: copolyimide; 4,4′-bis(3-aminophenoxy)biphenyl; melt processable)

INTRODUCTION

Aromatic polyimides[1] have marked thermal stability, and excellent mechanical, electrical and solvent resistance properties. Therefore, they are being used in such applications as automobile and aircraft parts and packaging in printed electronic circuitry. Aromatic polyimides synthesised from aromatic monomers generally possess excellent thermal stability and mechanical properties[2]. However, many of these polymers are insoluble and infusible, rendering them impossible to process by conventional methods, i.e. their processability was one of their drawbacks. Therefore, much effort has been expended on synthesising tractable polyimides that maintain reasonably high strength and thermal stability. Mainly, there are three methods to improve the processability of polyimides. One is the improvement of their solubility, worked on by Harris and Lanier[3] and other scientists[4]. They successfully produced several organo-soluble polyimides[5,6] by using aromatic monomers with bulky side-groups. The second is the improvement of solubility and thermoplasticity, worked on by Takekoshi and scientists of General Electric Co., (G.E.)[7] and then, they successfully produced and industrialised polyetherimides named as ULTEM™ having an excellent processability. The last method is the improvement of thermoplasticity. In order to improve thermoplasticity of polyimide, the National Aeronautics and Space Administration (NASA) and Mitsui Toatsu Chemicals, Inc. also tried to improve melt flowability of polyimide and then, they produced melt flowable polyimide, LARC#1500[8,9]. In order to improve thermoplasticity of polyimide, Yamaguchi and Ohta[10] investigated the relationship between chemical structures of polyimides and their *Tg* values by using bis(aminophenoxy)benzene (APB) isomers and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) as aromatic monomers, and reported that *Tg* values of obtained polyimides depended strongly on the amino-substituted position of the diamine monomers used. Systematic study of the relationship of chemical structure of polyimide based on diamine monomer structure, and its thermoplasticity was carried out by Tamai and Yamaguchi[11], and then several melt processable polyimides were introduced. Among these melt processable polyimides, polyimide obtained from 4,4′-bis(3-aminophenoxy)biphenyl (abbreviated to BAB) and pyromellitic dianhydride (PMDA) is currently receiving considerable attention[12–14] because of its outstanding thermal stability and melt processability. However, little is known about copolyimides obtained from BAB, therefore in this research work, copolyimides based on BAB and PMDA were synthesised with 4,4′-oxydianiline (4,4′-ODA) and/or 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), and their basic properties were investigated by focusing on their melt processability, thermal and crystallisation property.

EXPERIMENTAL

Starting materials

1,3-Dinitrobenzene and phthalic anhydride are products of Mitsui Toatsu Chemicals, Inc., N,N-Dimethylformamide (DMF), ferric chloride hexahydrate, hydrazine hydrate were obtained from Tokyo Kasei Kogyo Co., Ltd and used as received. Methylethylketone (MEK), isopropyl alcohol (IPA), m-cresol and γ-picoline were obtained from Kanto Chemicals., Ltd and used as received. 4,4′-Dihydroxybiphenyl was obtained from Honsyu Chemicals, Inc., 4,4′-diaminodiphenylether (4,4′-ODA) was received from Wakayama Seika Co., Ltd, pyromellitic dianhydride (PMDA) was obtained from Daicel Chemical Industries, Ltd., and 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA) was obtained from Mitsubishi Kasei Kogyo Co., Ltd and were used as received.

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Synthesis of 4,4'-bis(3-aminophenoxy)biphenyl (BAB)

BAB was synthesised according to the method of previous works[11,15] as follows. A 3 l five necked round bottom flask containing 186 g (1.0 mol) of 4,4'-dihydroxybiphenyl, 438 g(2.6 mol) of 1,3-dinitrobenzene, 363 g of potassium carbonate and 2000 ml of DMF were fitted with a mechanical stirrer, condenser, nitrogen pad and a thermometer. This mixture was heated to 145–150°C with stirring. After heating this mixture at 145–150°C for 16 h under nitrogen atmosphere, it was cooled down to ambient temperature. An insoluble inorganic residue was filtered off and filtrate was obtained. The filtrate was heated under a vacuum to distil off the solvent, cooled down to 65°C and then 2000 ml of methanol was added and stirred for 1 h. After cooling down to ambient temperature, precipitated brown crystal was collected by filtration, followed by washing with water and methanol and dried. The yield of 4,4'-bis(3-nitrophenoxy)biphenyl was 426 g (99.5% yield).

A 5 l five necked round bottom flask containing 426 g (0.98 mol) of crude 4,4'-bis(3-nitrophenoxy)biphenyl, 42.6 g of activated carbon, 4.3 g of ferric chloride hexahydrate and 2000 ml of ethyleneglycol monomethylether was fitted with a mechanical stirrer, condenser, nitrogen pad and a thermometer. This mixture was heating to reflux with stirring for 30 min and then 196 g (3.92 mol) of hydrazine hydrate was dropped into the mixture at 70–80°C over 3 h. Then this mixture was heated to 70–80°C for 5 h with stirring to complate the reaction. The reaction mixture was cooled down to ambient temperature, and then insoluble residue was filtered off. Obtained filtrate was poured into 2100 ml of water. The precipitated crystal was collected by filtration, and it was dissolved into a hot mixture of 205 g of 35% hydrochloric acid and 2300 ml of 50% aqueous IPA solution, and allowed to cool. The precipitated 4,4'-bis(3-aminophenoxy)biphenyl hydrochloride was filtered out and dissolved by warming into 2300 ml of 50% aqueous IPA solution, and filtered again after adding 20 g of activated carbon. The filtrate was neutralised with aqueous ammonia and precipitated crystal was filtered, washed with water and dried to yield 306.7 g (84.6%) of 4,4'-bis(3-aminophenoxy)biphenyl; m.p. 144–146°C; MS: 368 (M +), 340, 184; IR (KBr.cm^{-1}): 3400 and 3310 (amino group), 1240 (ether linkage). Elemental analysis calculated for $C_{24}H_{20}N_2O_2$: C 78.26%, H 5.43%, N 7.61%; found: C 78.56%, H 5.21%, N 7.66%.

Polymer synthesis

A typical procedure for polyimide and copolyimide synthesis was as follows. A mixture of 331.56 g (0.90 mol) of BAB, 20.02 g (0.10 mol) of 4,4'-ODA, 207.20 g (0.95 mol) of PMDA, 14.84 g (0.10 mol) of phthalic anhydride, 14 g of γ-picoline in 3500 g of m-cresol was stirred at 150°C for 4 h, and then cooled down, the reaction mixture was poured into MEK. The precipitated polymer was collected by filtration, followed by thorough washing with MEK and dried in a forced air oven to a temperature around the *Tg* of the polymer. The other polyimide and copolyimide powders were prepared by the same method as mentioned above.

MEASUREMENTS

The inherent viscosities (η's) of polymers were obtained at a concentration of 0.5% in a solvent (p-chlorophenol/phenol = 9/1 wt/wt) at 35°C. Glass transition temperatures (*Tg*'s) and melting temperatures (*T*m's) of polymers were determined using a Shimadzu 40 type differential scanning calorimeter (d.s.c) with a 16°C min^{-1} heating rate in N_2. The *Tg* value was taken at the inflection point of the ΔT *versus* temperature curve, and the *T*m value was taken at endothermic peak temperature from the d.s.c curve. Thermo-oxidative stability of polymer was estimated by 1% weight reduction temperature in air (*T*d1), using a Shimadzu 40 type thermogravimetric analyser (t.g.a.) with a 10°C min^{-1} heating rate. Melt-flow viscosity of polymer was determined by using a Flow-Tester (Shimadzu Flowtester CFT-500) setting an orifice with 1 mm diameter and 10 mm length, under 100 Kg cm^{-2} load at 380, 400 and 420°C. Crystallinity of polymer was estimated from wide angle X-ray diffraction (WAXS) data which was obtained on polymer powder and thin films. The X-ray diffractometer was operated at 50 KV and 200 mA using copper radiation source with a flat sample holder and a graphite monochromater. The density of 1 s counts was taken every 0.02° (2θ) and was recorded on hard disk for the angular of 5–50° (2θ). The degree of crystallinity of polymer was estimated from a diffractogram of the polymer sample compared with the diffraction halo of a quenched, fully amorphous sample as shown in *Figure 1*. Crystallisation rate of polymer was estimated as follows: fully amorphous thin polymer film was stored at 320°C under nitrogen in an oven so that displacement of nitrogen was controlled to 10 times per hour. Then, the degree of crystallinity of sample estimated by WAXS was measured *versus* storage time.

RESULTS AND DISCUSSION

Synthesis procedure of BAB was shown in *Scheme 1*. BAB

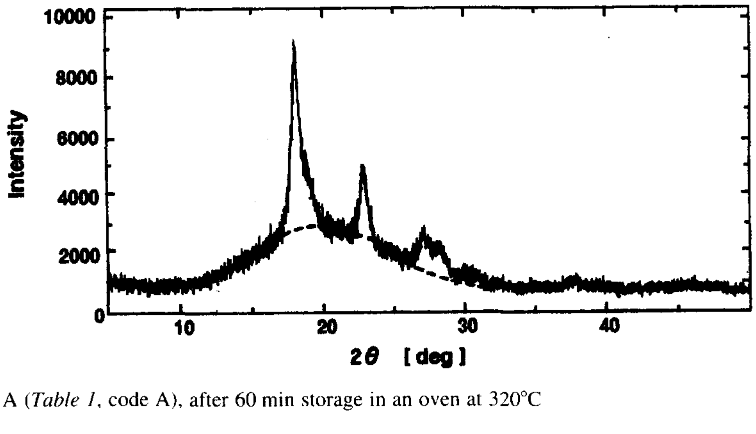
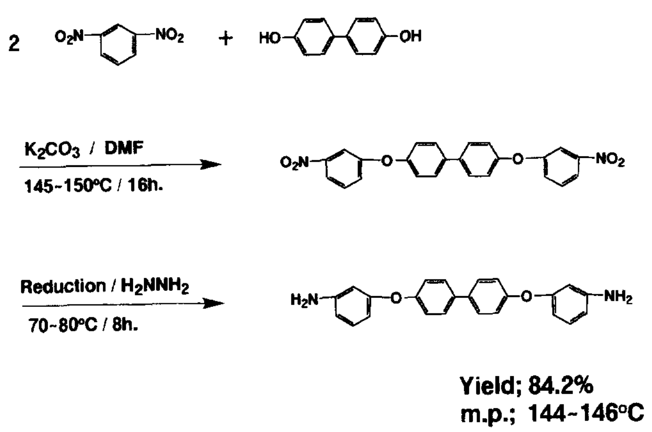


Figure 1 WAXS of polyimide A (*Table 1*, code A), after 60 min storage in an oven at 320°C



Scheme 1

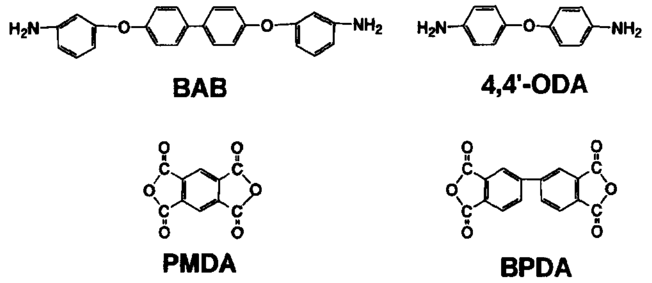


Figure 2 Chemical structures of monomers used for polymer synthesis

was synthesised from 4,4′-dihydroxybiphenyl and 1,3-dinitrobenzene followed by reduction. Yield of BAB based on 4,4′-dihydroxybiphenyl was 84.2%.

Chemical structures of monomers used for polymer synthesis and their abbreviated names are summarised in *Figure 2*.

Polyimides and copolyimides were synthesised in heating m-cresol containing γ-picoline catalyst at 150°C for 4 h according to the previous method[8] in our laboratory. Sample codes of synthesised polyimides and copolyimides, and their monomer compositions are summarised in *Table 1*.

Basic properties of synthesised polymers are summarised in *Table 2*. η's of synthesised polymers were controlled to 0.47~0.53 dl/g by selecting the optimum mole ratio of tetracarboxylic dianhydride and diamine, and polymer chain end was terminated by using phthalic anhydride as an end-capper. A and K were polyimides, therefore these polymers were references. B–F were copolyimides synthesised from BAB, 4,4′-ODA and PMDA. G–J were also copolyimides synthesised from BAB, PMDA and BPDA.

Table 1 Monomer compostions and sample codes

Sample codes	BAB[a] (mol%)	4,4′ODA[b] (mol%)	PMDA[c] (mol%)	BPDA[d] (mol%)
A	100	0	100	0
B	98	2	100	0
C	95	5	100	0
D	90	10	100	0
E	87	13	100	0
F	70	30	100	0
G	100	0	90	10
H	100	0	80	20
I	100	0	50	50
J	100	0	20	80
K	100	0	0	100

[a] 4,4′-bis(3-aminophenoxy)biphenyl
[b] 4,4′-oxydianiline
[c] Pyromellitic dianhydride
[d] 3,3′,4,4′-biphenyl tetracarboxylic dianhydride

Table 2 Basic properties of synthesized polyimides and copolyimides

Sample codes	η[a] (dl/g)	Tg[b] (°C)	Tm[b] (°C)	Td1[c] (°C)
A	0.48	250	388	517
B	0.50	248	N.D.[d]	515
C	0.51	248	N.D.	501
D	0.50	252	N.D.	508
E	0.51	253	N.D.	510
F	0.50	249	N.D.	514
G	0.47	246	N.D.	503
H	0.47	239	N.D.	514
I	0.52	232	N.D.	527
J	0.53	229	N.D.	529
K	0.50	225	N.D.	536

[a] Inherent viscosity was measured at a concentration of 0.5% in a solvent (p-chlorophenol/phenol = 9/1) on the weight basis) at 35°C
[b] d.s.c. at a heating rate of 16°C min^{-1}
[c] Temperature where the sample loss 1% of its weight under air atmosphere measured by t.g.a.
[d] Not detected

It was known that polyimide obtained from 4,4′-ODA and PMDA did not show clear inflection point of *Tg* by d.s.c. measurement, however, in the case of B–F copolyimides, their *Tg*'s were observed and ranged from 248 to 253°C, and these values were almost the same as 250°C—that is the *Tg* of polyimide A synthesised from BAB and PMDA. Polyimide A showed *Tm* at 388°C, however B–F copolyimides did not show *Tm* values. *Td*1 values of B–F ranged from 508 to 515°C, and that of polyimide A was 517°C. These values did not show clear difference. *Td*1 value shows temperature where the sample loss is 1% of its weight under air atmosphere, therefore thermo-oxidative stability of the sample can be eatimated from this value. This result means thermo-oxidative stabilities of copolyimides B–F are almost the same as that of polyimide A. From these comparisons, it was found that basic thermal properties of B–F copolyimides were almost the same as that of polyimide A except for the existence of *Tm* value.

In the case of G–J copolyimides, *Tg*'s ranged from 246 to 229°C and tended to decrease in the order G > H > I > J. *Tg*'s of polyimide A and K were 250°C and 225°C respectively, therefore lower *Tg* can be attributed to the contents of BPDA unit in a repeating structure of polymer. This result indicates that *Tg* of copolyimide synthesised from BAB, PMDA and BPDA are decreasing according to the increase of BPDA contents in a repeating unit of copolyimide. *Tm*'s were not detected in the case of G–J copolyimides and polyimide K. *Td*1 values of G–J copolyimides ranged from 503 to 529°C. *Td*1 values of G–J tended to increase in the order G < J, however its tendency was not so clear, because *Td*1 values of A and K were 517°C and 536°C, respectively.

Melt-flow viscosities of polyimides [A, K] and copolyimides [B–F, G–J] at 380, 400 and 420°C are summarised in *Table 3*. A, B and F were not melt flowable at 380°C. Polyimide A synthesised from BAB and PMDA has *Tm* at 388°C as shown in *Table 2*, therefore it can not be melt flowable at 380°C because measurement temperature was lower than its *Tm* value. *Figure 3* shows the relationship between 4,4′-ODA unit contents in a repeating structure of

Table 3 Melt-flow viscosities of polyimides and copolyimides

Sample codes	Melt-flow viscosity (Pa.sec)[a] Measurement temperature (°C)		
	380	400	420
A	N.F.[b]	760	430
B	N.F.[b]	870	460
C	1910	810	470
D	1320	720	470
E	1900	910	510
F	N.F.[b]	10200	2670
G	—[c]	—[c]	410
H	—[c]	—[c]	390
I	—[c]	—[c]	350
J	—[c]	—[c]	360
K	—[c]	—[c]	350

[a]Measured by using a flow-tester setting an oriface with 1 mm diameter and 10 mm length, under 100 kg cm^{-2} load.
[b]Did not melt-flow
[c]Did not measure

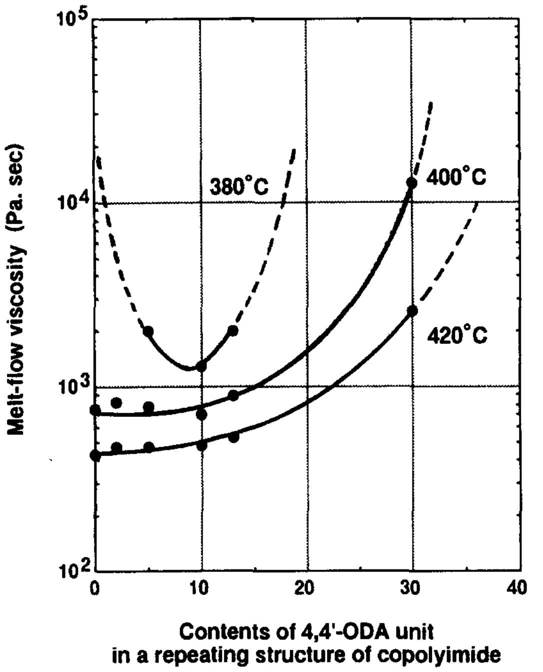


Figure 3 Melt-flow viscosity *versus* contents of 4,4'-ODA unit in a repeating structure of copolymide

B–F copolyimides and their melt-flow viscosities at 380, 400 and 420°C. 0% contents of 4,4'-ODA means polyimide A. As shown in *Figure 3*, melt-flow viscosity value was increasing according to increase of 4,4'-ODA unit contents in a repeating unit at 400 and 420°C. It is assumed that increase of 4,4'-ODA contents in a repeating unit means that 4,4'-ODA/PMDA unit is increasing in copolyimide structure, as it is well known that polyimide obtained from 4,4'-ODA and PMDA is infusible polyimide, therefore the melt-flow viscosity value of copolyimide was increasing according to the increase of 4,4'-ODA contents in a repeating unit.

In the case of measurement at 380°C, copolyimide D having 10% contents of 4,4'-ODA showed the lowest value of melt-flow viscosity. As mentioned above, polyimide A having 0% contents of 4,4'-ODA unit could not be melt flowable at 380°C, and melt-flow property of copolyimide having lower than 10% contents of 4,4'-ODA unit was assumed to be similar to that of polyimide A. Therefore melt-flow viscosity of copoyimide at 380°C was decreasing between 0 and 10% contents of 4,4'-ODA in a repeating unit. Melt-flow viscosities of G–J copolyimides ranged from 350 to 410 Pa.sec at 420°C. BPDA unit contents in a repeating unit of G–J copolyimides and their *Tg*'s showed good corelation as shown in *Table 2*, however their melt viscosities at 420°C did not show a big difference among these copolyimides.

As mentioned above, in the case of copolyimides obtained from BAB, PMDA and 4,4'-ODA, their *Tg* values did not show clear difference between 0 and 30 mol% of 4,4'-ODA contents, however their melt viscosities were drastically changed.

On the other hand, in the case of copolyimides obtained from BAB, PMDA and BPDA, their *Tg* values were decreasing according to the increase of BPDA contents in a repeating structure unit, however their melt viscosities did not show a clear difference. These different effects of copolymerised components such as 4,4'-ODA and BPDA on the properties of obtained copolyimides were assumed to be caused by the different properties of copolymerised units such as 4,4'-ODA/PMDA unit and BAB/BPDA unit.

It was well known that polyimide A obtained from BAB and PMDA had an excellent thermal stability because of its high *Tg* and *Tm* values[16–18]. Existence of *Tm* by d.s.c. measurement means the polymer has crystallisation property. In this research work, the crystallisation properties of copolyimides based on BAB and PMDA were also investigated. As shown in *Table 2*, polymers except for polyimide A did not show *Tm* values under the measurement condition by d.s.c. at a 16°C min^{-1} heating rate, therefore in order to investigate the crystallisation property of copolyimide, the difference of crystallisation rate was studied. First of all, fully amorphous polymer films were prepared by heating the polymer powder at 420°C for 5 min under 100 kg cm^{-2} G pressure followed by a quenching at a 60°C sec^{-1} rate to ambient temperature. Thickness of obtained films were 50–70 μm. Obtained fully amorphous polymer was stored at 320°C under nitrogen atmosphere, and then the degree of crystallinity of the sample estimated by WAXS was measured *versus* storage time as mentioned in measurement columns. 320°C was selected as the test temperature for estimation of crystallisation rate of polymer, because Tamai and Ohta reported in their patents[19–21] that crystallisation temperature (*Tc*) of polyimide A which was taken at exothermic peak temperature from the d.s.c. curve was 330°C. *Figure 4* shows the

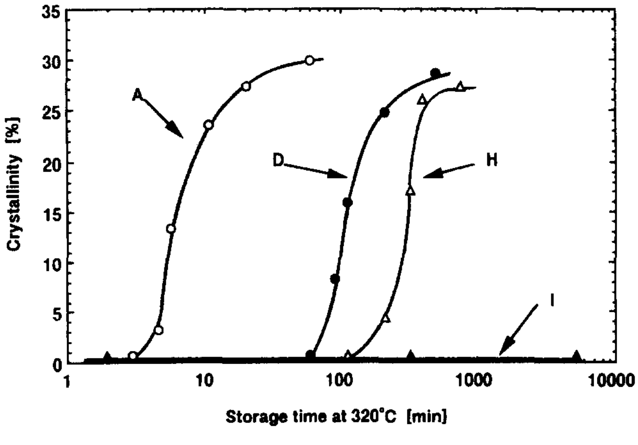


Figure 4 Crystallization behaviour of copolymides based on 4,4'-bis(3-aminophenoxy)biphenyl

crystallisation behaviour of several copolyimides stored at 320°C. The degree of crystallinity of D, H, I and polyimide A estimated by WAXS was measured *versus* storage time at 320°C and are summarised in this figure. Storage time of initial observation of crystallinity of A, D and H were 5 min, 50 min and 100 min respectively. Copolyimide I having 50% contents of BPDA unit did not show crystallinity before 5000 min storage time. It was therefore assumed that the beginning of crystallisation would be delayed by increasing contents of copolymised compounds such as 4,4′-ODA and BPDA. However, final crystallinities of D and H were 28% and 27% respectively. This result suggests that crystallisation rate of polyimide A is delayed by copolymerising the other components such as 4,4′-ODA and BPDA.

SUMMARY AND CONCLUSIONS

Copolyimides based on 4,4′-bis(3-aminophenoxy)biphenyl (BAB) and pyromellitic dianhydride (PMDA) were synthesised with 4,4′-oxydianilline (4,4′-ODA) and/or 3,3′4,4′-biphenyl tetracarboxylic dianhydride (BPDA) and then the basic property and melt processability of these copolyimides were investigated. Basic thermal property such as glass transition temperature (*T*g) and thermo-oxidative stability of copolyimides obtained from BAB, PMDA and 4,4′-ODA were almost at the same level, however the melt processability was different. Melt-flow viscosity of copolyimide obtained from BAB, PMDA and 4,4′-ODA increased according to the increase of 4,4′-ODA contents in a repeating structure unit of copolyimide. *T*g of copolyimide obtained from BAB, PMDA and BPDA tended to decrease according to the increase of BPDA contents in a repeating unit of copolyimide, however, its melt-flow viscosity at 420°C did not strongly depend on BPDA contents in a repeating structure unit. Crystallisation rate of copolyimide was basically delaying by increasing the contents of copolymised compounds such as 4,4′-ODA and BPDA.

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